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STANDARDS OF PERFORMANCE FOR NEW AND SUBSTANTIALLY MODIFIED NITRIC ACID PLANTS

ENVIRONMENTAL PROTECTION AGENCY

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FOR NEW AND SUBSTANTIALLY MODIFIED NITRIC ACID PLANTS

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Bureau of Stationary Source Pollution Control
Division of Compliance
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This document covers performance standards for facilities producing so-termed "weak nitric acid" (defined as 55-70 percent strength). It does not apply to the various processes used to produce strong acid by extraction or evaporation of weak acid or by the direct strong acid process.

Nitric acid production facilities can discharge oxides of nitrogen--principally nitrogen oxide and nitrogen dioxide--as well as acid mist and reducing compounds such as carbon monoxide. At this time, standards of performance are being established only for total oxides of nitrogen and for attendant visible emissions which are a function of the nitrogen dioxide concentration. For the purpose of the standards, all oxides of nitrogen (NO_x) shall be measured and reported as nitrogen dioxide (NO_2). The standards do not include any "non-criteria pollutants" as defined by Section 111(d) of the Act; therefore, they do not require the establishment of State emission standards for existing sources pursuant to that Section.

The standards are:

(a) 3.0 pounds of NO_x per ton of acid produced or 1.5 kilogram NO_x per metric ton. Acid production is expressed in tons of equivalent 100% strong nitric acid. Acid actually produced is 55-70 percent strength.

(b) Visible air pollutants shall not be released to the atmosphere except for two minutes in any one hour of operation. These emission limits shall apply for all periods of operation except for the first four hours following startup.

For a typical nitric acid plant where there is no dilution of exit gases, 3.0 pounds of NO_x per ton is equivalent to an exit gas concentration of 209 parts per million NO_x by volume. The visible emission standard is

compatible with the NO_x standard. If NO_x emissions are held at or below 209 ppm, there will be essentially no visible emissions from the facility. These performance standards apply to any nitric acid production facility, the construction or modification of which is commenced after July 29, 1971. Since construction of such facility requires 18 to 24 months, the first plants to be affected by the standard will not be operated until at least 1973.

The performance standards also apply to any existing facility which is physically modified or which undergoes changes in the method of operation such that the hourly production rate of nitric acid or the emission rate of NO_x is increased by more than 10 percent above the maximum production rate or the maximum NO_x emission level prior to July 29, 1971.

The replacement or reconstruction of more than 50 percent of any existing facility will be considered new construction subject to the performance standard.

It has been demonstrated that conventional nitric acid plants can be operated consistently at or below the limits of the standards using catalytic decomposition systems. Pressure, temperature, residence time, and reactant concentrations in the system are controlled such that the bulk of the NO and NO_2 is decomposed to nitrogen and oxygen. The standards are based on actual tests and take into consideration the fact that there are interferences which cause NO_x emissions to be greater during abnormal periods of operation. In fact, a system designed to meet this standard at all times will operate at a considerably lower NO_x level much of the time.

The NO_x standard is based on catalytic decomposition systems using natural gas as fuel. This represents a more severe condition of operation and generally higher discharges of NO_x than is experienced when hydrogen fuels are used in the decomposition system. The use of hydrogen is feasible only when the nitric acid plant is operated in proximity to a hydrogen source. When hydrogen is employed, exhaust gases are generally below 150 ppm NO_x.

At the present time, there are no other methods of controlling NO_x from nitric acid plants that have been adequately demonstrated. A most promising avenue of control appears to be through the use of molecular sieves. Utilizing these devices on a small pilot plant scale, almost all oxides of nitrogen have been removed from acid plant stack gas such that emissions of 0.2 to 0.7 pounds NO_x per ton of acid (10 to 50 ppm) are released to the atmosphere. The sieves are regenerated with NO_x and dilute nitric acid recycled back to the acid production system. If molecular sieves are shown to be adaptable to nitric acid production facilities, it is expected that a performance standard of 0.7 pounds of NO_x per ton of acid could be justified. When molecular sieves or other improved NO_x control systems are adequately demonstrated, these standards of performance will be revised to reflect the lower emissions.

While there may be other air pollutants discharged from nitric acid production facilities, it is not deemed appropriate to establish standards for them at this time. They include nitric acid mist and reduced compounds. Acid mist is a problem only where NO_x is not controlled. When catalytic decomposition systems are applied to nitric

acid facilities, it is necessary to control acid mist stringently to prevent catalyst fouling. This would also be true if molecular sieves were utilized in lieu of catalytic decomposition systems. In order for the sieves to function properly and to prevent sieve damage, it would be necessary to remove essentially all of the acid mist upstream of the molecular sieves.

Reducing compounds are by-products of the catalytic control systems. Compounds such as carbon monoxide, hydrocarbons, and hydrogen cyanide can be formed in the catalytic unit if reducing conditions are overly severe. In such instances, the NO_x emissions are usually extremely low. While information is lacking in this area, there have been no indications that emissions of reduced compounds are of sufficient magnitude to warrant a standard. Nevertheless, measurements will be conducted and carbon monoxide instruments will be required on new installations. If significant quantities of reduced compounds are found to exist, performance standards may be required. Should molecular sieves be employed in place of the catalytic systems, no reduced compounds would be expected in the exit gases.

The purpose of requiring continuous NO_x and carbon monoxide monitoring is (1) to provide a record of performance and (2) to provide intelligence to plant operating personnel such that suitable corrections can be made when the system is shown to be out of adjustment. Operators will be required to maintain the monitoring equipment in calibration and to furnish records of NO_x values and of carbon monoxide values to the Administrator of EPA or to the responsible State agency. Carbon monoxide

monitoring is required only with catalytic decomposition systems and with similar devices where reducing atmospheres are encountered.

New source performance standards for all source categories will be reviewed from time to time. The limits may be revised depending upon new control technology which becomes available and is adequately demonstrated. Revisions could include the addition of limits for further pollutants as well as revision in thepresent standards for NO_x and visible emissions.

The costs of catalytic decomposition systems have been considered in setting these performance standards. For a modern plant of 300 tons per day capacity, the addition of a two-stage catalytic decomposition system represents eight percent of the costs of the total facility. It raises the operating costs of such a plant by five percent but represents only a one percent increase in the price of the most typical product, ammonium nitrate fertilizer. Single-stage systems are less costly to install and operate than two-stage catalytic systems.

NITRIC ACID PLANT LOG

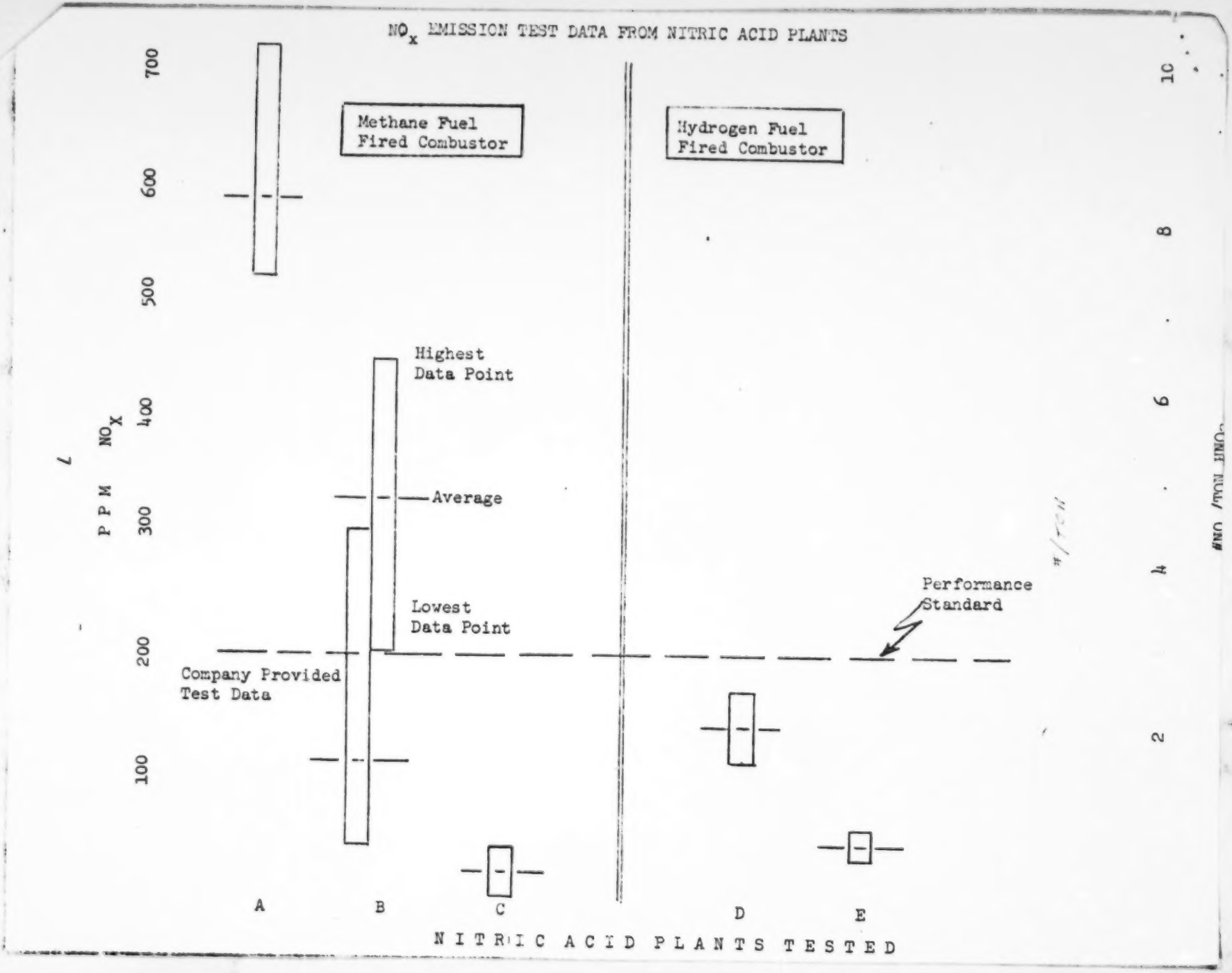
A. 350 ton per day design capacity. During test period acid production was 125% of design. Abatement device: Natural gas fired, dual stage (honeycomb catalyst) catalytic combustor.

B. 155 ton per day design capacity. During test period acid production was 100% of design. Abatement device: Natural gas fired, single stage (pelletized catalyst) catalytic combustor.

C. 350 ton per day design capacity. During test period acid production was 107% of design. Abatement device: Natural gas fired, dual stage (pelletized catalyst) catalytic combustor.

D. 55 ton per day design capacity. During test period acid production was 127% of design. Abatement device: Ammonia plant purge gas (65% hydrogen) fired single stage (pelletized catalyst) catalytic combustor.

E. 55 ton per day design capacity. During test period acid production was 100% of design. Abatement device: Ammonia plant purge gas (65% hydrogen) fired single stage (pelletized catalyst) catalytic combustor.


NO_x EMISSION TEST DATA FROM NITRIC ACID PLANTS
Methane Fuel Fired Combustor
Hydrogen Fuel Fired Combustor
PPM NO_x
700
600
500
400
300
200
100
Highest Data Point
Average
Lowest Data Point
Performance Standard
Company Provided Test Data
A
B
C
D
E
NITRIC ACID PLANTS TESTED